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Transduction in semiconducting metal oxide based gas sensors - implications of the conduction mechanism

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Abstract

For chemoresistive sensors based on semiconducting metal oxides the conduction mechanism in the sensing layer has a very large impact on the magnitude and even on the direction of the sensor signal. That means that for very similar surface reactivity (reception function) the translation of the surface charge transfer processes into sensor resistance changes (transduction function) can be very different. This idea is illustrated with the example of the different sensor signals for different conduction types, *n* and *p* and with the example of the change of sensor signal direction determined by the change of the conduction type under various ambient atmospheres.

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Gas sensors; conduction modeling; reception/transduction; morphology

1. Introduction

Chemoresistive gas sensors based on Semiconducting Metal OXides (SMOX) are widely used in applications spanning from natural gas leaks alarms to automotive (in-cabin air quality control) to complex chemical sensor systems [1]. The most successful materials are SnO₂ and WO₃, which are both n-type semiconductors and currently used in commercial devices. For the state of the art sensors, using porous and thick sensing films - realized by screen printing or drop coating - looks like being the approach of choice. The reason, as explained in [2], is the fact that such a morphology has the advantage of: providing easy access to the whole of the sensitive material; ensuring the largest impact of the surface phenomena onto the resistance of the sensing layer; minimizing the electrical effect of the electrodes. For p-type materials, it was shown recently that such a morphology is not the most appropriate to translate their considerable surface reactivity into large sensor signals [3]. All of that, points out at the essential role

played by the conduction in the sensing layer in gas sensing with SMOX based devices. In this contribution a few cases illustrating this idea will be discussed.

2. Conduction in the Sensing Layer

The SMOX based gas sensors are fabricated by the deposition of a sensing layer over a substrate provided with electrodes, for the read out of the electrical resistance, on the front side and a heater on the backside. The latter is needed to allow for the heating at an operation temperature, usually, in the range 150 to 500°C. An example is shown in Fig 1.

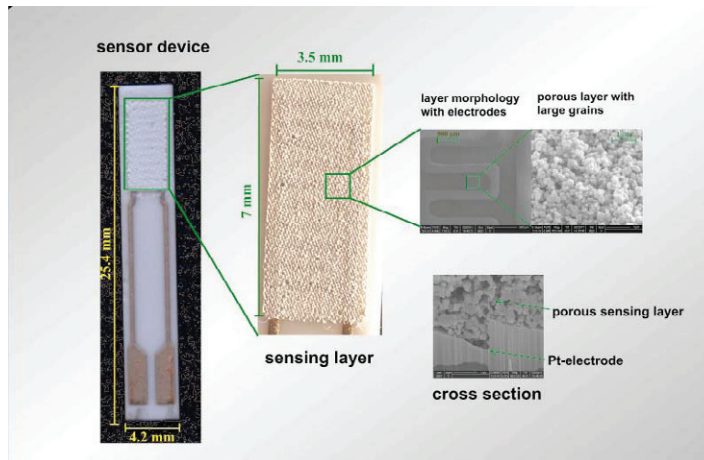


Fig. 1. Sensor samples used in the author's group; the porous thick film sensing layer is deposited by screen-printing, the electrodes and the heater are thick film Pt-layers also screen-printed over the alumina substrate. The dimensions are optimized for the *Operando* studies instrumentation.

2.1. Difference between *n* and *p*-type SMOX

The reasons of the differences between *n* and *p*-type SMOX are easy to understand by looking at the schematic representations of the sensing layer for the two cases shown in Fig 2; there, very comparable grain sizes and depletion/accumulation layer dimensions were considered in order to allow for a straightforward comparison. The different band gaps are qualitatively corresponding to SnO₂ and CuO. The difference between the sensor responses of the different type of materials is related to the fact that oxygen ionosorption has quite different effects:

For the *n*-type material it builds a surface depletion layer, which has a lower concentration of free charge carriers (electrons) and by that a higher resistivity. The electron transport in the layer will take place from one grain to the other over the grain-grain barrier; simply put, “perpendicular” to the surface. If one assumes the Schottky approximation to be valid, meaning negligible concentration of electrons in the depletion layer, one can write the following relation between the layer resistance and the surface band bending V_S :

$$R_n \approx \exp(qV_S/kT) \quad (1)$$

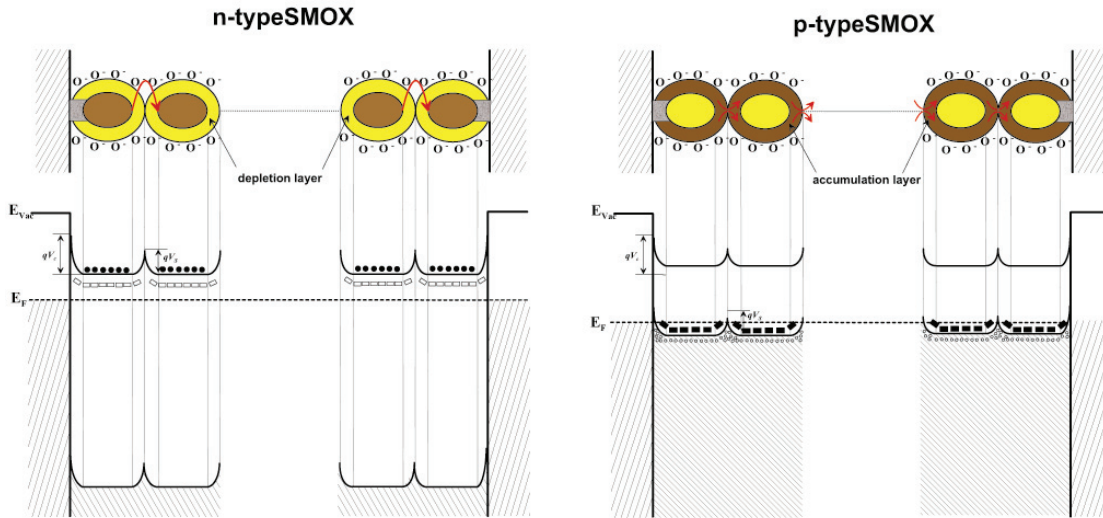


Fig. 2 Cartoon-like illustration of the conduction processes and the corresponding energy bands for a n-type SMOX material (left) described by a depletion layer and for a p-type SMOX material (right) with accumulation layer.

For the *p*-type material the effect of oxygen ionosorption is the appearance of a surface accumulation layer, which has a higher concentration of free charge carriers (holes) and by that a lower resistivity. That means that it will be possible to have a lower resistance path around the grains and “parallel” to the surface. The relation between the resistance and the surface band bending is [4]:

$$R_p \approx \exp(qV_s/2kT) \quad (2)$$

By comparing the two dependencies presented in (1) and (2) one can easily see that the same change in band bending, meaning the same surface reactivity, will determine different changes of the electrical resistance, meaning different sensor signals. By defining the sensor signal as the relative change of the electrical resistance, one has the following relation between the sensor signals in the two cases:

$$(S_p)^2 = S_n \quad (3)$$

This shows that a different type of conduction mechanism will determine a very different sensor signal for the same surface reactivity.

2.2. Inversion of type of conduction

In the case of $\alpha\text{-Fe}_2\text{O}_3$, which is a *n*-type semiconductor, one records a change of conduction type at the surface because of the oxygen ionosorption [5]. This phenomenon brings about an inverted type of sensor response: the resistance increases during exposure to low concentrations of reducing gases and decreases when the concentrations are further increased.

Fig 3 shows the results of simultaneous DC electrical resistance and work function changes measurements; one can observe the transition between dominant *p*-type conduction (AB region) to dominant *n*-type conduction (BC region).

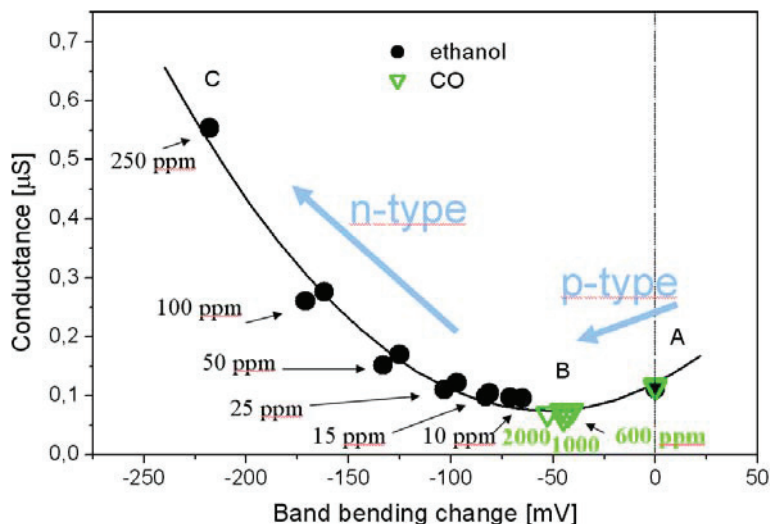


Fig. 3 The conductance of α -Fe₂O₃ sensor as a function of the band bending change determined by simultaneous work function and conductivity measurements at $\approx 320^\circ\text{C}$

It is clear from that even if the effect of the reaction with the reducing gases was all the time the same - reducing of the surface negative charge demonstrated by the decrease of the surface band bending - the electronic effect of change of conduction type did determine different sensor signals.

3. Conclusion and Outlook

The examples presented above are clearly showing the importance of the conduction mechanism for the magnitude and, in special cases, even the direction of the sensor signal. In the presentation some additional examples will be provided that show the effect of the change from depletion layer controlled to accumulation layer controlled electrical transport properties in the sensing layer.

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